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# Continuous-wave two-photon excitation of individual CdS nanocrystallites

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By use of low-temperature confocal microscopy, continuous-wave two-photon fluorescence images are obtained of individual CdS nanocrystallites embedded in a polymer matrix. The quadratic dependence of the emission rate on the applied laser power proves that the observed fluorescence originates from the simultaneous absorption of two photons. From the experimental data the two-photon absorption cross-section  $\sigma^{(2)}$  could be determined, resulting in a value smaller than that known from literature. The work presented is a first step towards high-resolution fluorescence-excitation spectroscopy on the electronic states in the band edge, inaccessible by conventional one-photon spectroscopy. © 2001 American Institute of Physics.

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Nanometer-sized semiconductor crystallites have attracted considerable attention over the last decade owing to their unique physical properties that depend sensitively on size and shape, and their potential use for a wide range of applications.<sup>1–3</sup> When the size of a nanocrystallite is reduced to dimensions in the range of or smaller than the bulk exciton radius, the electronic level structure changes appreciably as a result of the confinement of the charge carriers in all three dimensions. This quantum confinement effect causes a shift of the absorption threshold to higher energies and a transition from broad structureless energy bands to discrete energy levels. The associated concentration of oscillator strength into electronic transitions to discrete states at the edge of the conduction band causes semiconductor nanocrystallites to be potentially useful for new and emerging technologies, such as optical switches.<sup>4</sup> In order to make the best use of these systems, precise knowledge of the electronic structure is required.

A major obstacle in studies of ensembles of nanocrystallites is the size distribution of the particles which averages spectral features and dynamical properties. In efforts to overcome this problem, hole-burning,<sup>5</sup> photon-echo,<sup>6</sup> and fluorescence line-narrowing<sup>7</sup> spectroscopies have been applied but, while restricting the size distribution, still a large number of nanocrystallites is present in the sampled volumes. This ensemble averaging can be removed by investigating single nanocrystallites, allowing a more direct insight into the optical properties and the electronic states of the particle. The wealth of spectral information obtained by the application of high-resolution fluorescence-excitation spectroscopy on individual quantum systems<sup>8–10</sup> in recent years suggests its applicability to CdS nanocrystallites to unravel the spec-

tral properties of the lowest excited states in great detail. Recently, first observations of the emission and the emission spectra of single CdSe<sup>11–13</sup> and CdS<sup>14,15</sup> nanocrystallites have been published. However, it is not possible to perform one-photon excitation spectroscopy in the wavelength region corresponding to the band gap of the CdS nanocrystallites because the luminescence occurs mainly in the same wavelength region (see Fig. 1). Emission spectroscopy by excitation high above the band gap and by subsequent analysis of the emission light with a monochromator suffers from a relatively low spectral resolution and the linewidths measured are limited by the bandwidth of monochromators.<sup>12,15</sup> An alternative way to obtain high-resolution spectral information about the lowest excited states of single semiconductor nanocrystallites would be the application of two-photon excitation techniques using continuous-wave single-mode lasers. Here the idea is to use light of energy equal to (or slightly greater than) one half the band gap energy to create an electron-hole pair by the simultaneous absorption of two photons. Pulsed two-photon excitation has recently been ap-

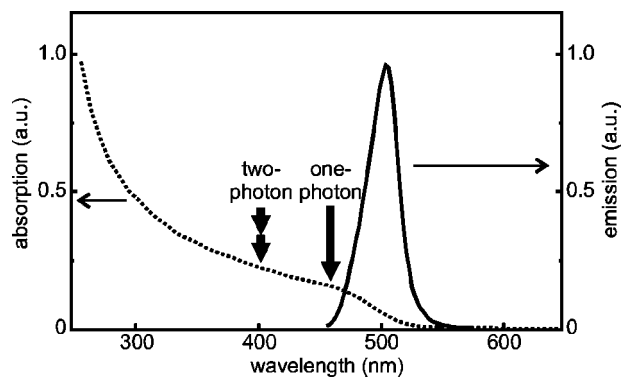


FIG. 1. The room-temperature absorption (dashed curve) and emission (solid curve) spectra of a sample of CdS nanocrystallites. The vertical single and double arrows indicate the excitation wavelength for the one- and two-photon microscopy, respectively.

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plied to monitor the emission from individual CdSe nanocrystallites.<sup>11,16</sup> The extremely high peak power in pulsed excitation is used to induce the two-photon absorption events that are highly improbable due to the low two-photon absorption cross sections of the nanocrystallites. A drawback is that the Fourier-transformed spectral width of, for instance, picosecond pulses would limit the spectral resolution attainable in this type of fluorescence-excitation spectroscopy to several tens of gigahertz, whereas the linewidth of the lowest transition of the exciton in the CdS nanocrystallites may be of the order of a few megahertz. Here we report the successful confocal imaging of the fluorescence of individual CdS nanocrystallites by two-photon excitation with a single-mode continuous-wave laser source (spectral linewidth  $\leq 1$  MHz). These experiments pave the way for high-resolution fluorescence-excitation spectroscopy on single semiconductor particles.

The preparation of CdS nanocrystallites in an aqueous solution is described in detail elsewhere.<sup>17</sup> In all experiments described in this letter particles were used with a mean diameter of 5 nm, containing approximately  $10^3$  atoms. An emission and absorption spectrum of the colloidal CdS solution is shown in Fig. 1. Thin polymer films with an estimated thickness of less than  $1 \mu\text{m}$  were prepared by spin coating a solution of demineralized water with 0.5% (w/w) poly(vinyl alcohol) (PVA) ( $M_w = 125\,000$ ) and  $5 \times 10^{-11}$  M CdS particles on a quartz substrate. The sample was mounted in a helium bath cryostat together with a commercial microscope objective (numerical aperture=0.9) and cooled down to 1.2 K. Fluorescence microscopy was performed with a home-built beam-scanning confocal microscope with a scan range of  $50 \times 50 \mu\text{m}^2$  at low temperature. For the one-photon microscopy the 457.9 nm line of an  $\text{Ar}^+$  laser was used for excitation. A single-mode continuous-wave titanium:sapphire laser served as excitation source for the two-photon experiments. In order to generate sufficient two-photon absorption events to allow for detection of the fluorescence, the excitation intensity could be increased to a continuous-wave intensity of  $50 \text{ MW/cm}^2$  without causing appreciable heating effects in the sample. After separation from scattered excitation light by means of a dichroic mirror and appropriate color filters, the fluorescence photons were detected using an avalanche photodiode.

Figure 2(a) shows an image of CdS nanocrystallites embedded in a spin-coated PVA film after excitation with light with a wavelength of 810 nm at an intensity of  $6 \text{ MW/cm}^2$ . The excitation wavelength of 810 nm corresponds to two-photon transitions at 405 nm, at the high-energy side of the absorption onset (as indicated in Fig. 1 by the double arrow). The same sample area was imaged again [Fig. 2(b)] by detecting the fluorescence after one-photon excitation at 457.9 nm. In both images, similar structures and dots are present. The observation of discrete on/off blinking of the fluorescence of the dots, both for one-photon and two-photon excitation, identifies the dots in the images as single CdS nanocrystallites [Fig. 2(c)].

The photon count rate in Fig. 2(c) does not show pure on/off behavior. It is known that the fluctuation in the fluorescence intensity of nanocrystallites are caused by two types of processes. Auger ionization of the particle with subse-

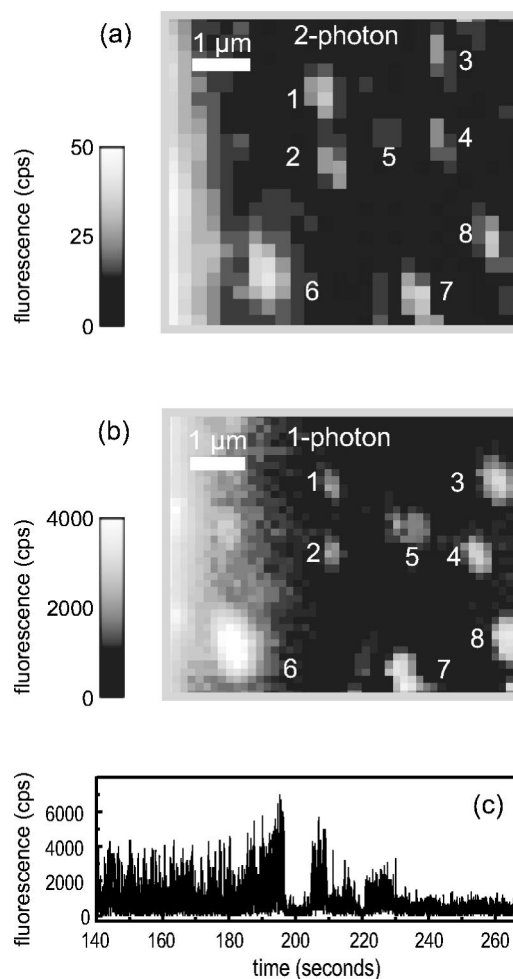


FIG. 2. (a) A fluorescence image ( $6 \times 6 \mu\text{m}^2$ ) of a sample of CdS nanocrystallites in a layer of PVA spin coated on a quartz substrate. The fluorescence is obtained by a continuous-wave, two-photon excitation of the CdS particles at an excitation intensity of  $6 \text{ MW/cm}^2$  and a wavelength of 810 nm. The large white area at the left side corresponds to a clustering of a large number of CdS nanocrystallites, whereas the small numbered dots stem from individual particles. (b) The same area of the sample area depicted in (a), obtained by one-photon excitation of the CdS nanocrystallites at an excitation intensity of  $1.2 \text{ kW/cm}^2$  and a wavelength of 457.9 nm. Comparison with the two-photon image in (a) reveals the presence of the same structures and dots. The chromatic aberration, caused by the large difference in excitation wavelengths between (a) and (b), causes the magnification of the optical system for both cases to be slightly different, thereby explaining the slight mismatch in position of the individual features. (c) The fluorescence-time trace, after one-photon excitation, of one of the bright dots visible in the fluorescence images. The on-and-off behavior (blinking) is typical for single quantum systems.

quent trapping will give rise to a telegraph-like on/off behavior of the emission.<sup>18</sup> At low temperature, however, spectral diffusion of the transitions<sup>19,20</sup> through the excitation line results in nondiscrete fluctuations of the intensity due to the Lorentzian line shape of the transition. This behavior has already been reported by Koberling *et al.*<sup>21</sup> and has recently been discussed explicitly by Neuhauser *et al.*<sup>22</sup>

The transition probability for simultaneous two-photon absorption depends on the square of the incident light intensity. When the CdS nanocrystallites are represented by a simple two-level system without any dark states influencing the emission intensity, the count rate  $R$  is given by<sup>23</sup>

$$R = A_{\text{tot}} \sigma^{(2)} \left( \frac{I}{\hbar \omega} \right)^2, \quad (1)$$

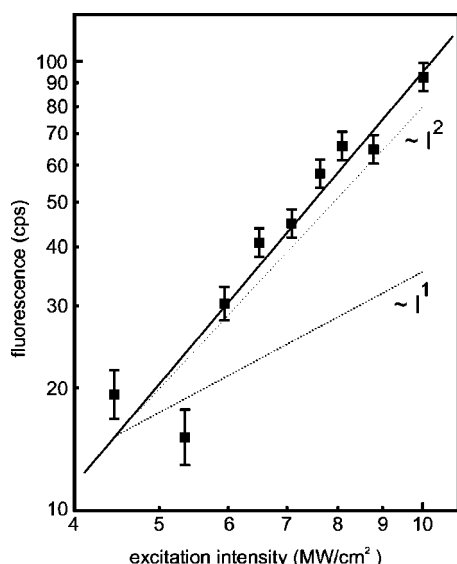


FIG. 3. The detected fluorescence intensity of a single CdS nanocrystallite, obtained by means of two-photon excitation, as a function of the excitation intensity  $I$ . A fit of the experimental data with a power law (solid line) reveals a proportionality to  $I$  to the power  $2.2 \pm 0.1$ . The dashed lines  $\sim I^1$  and  $\sim I^2$  are shown for comparison.

where  $A_{\text{tot}}$  represents the total collection efficiency of the setup,  $\sigma^{(2)}$  is the two-photon absorption cross section,  $I$  is the excitation intensity, and  $\hbar\omega$  is the energy of the incident photons. Indeed a quadratic intensity dependence on  $I$  is observed for the emission of the single nanocrystallites, while the background signal shows a linear intensity dependence. Figure 3 shows the log-log plot of the detected fluorescence signal of a single CdS nanocrystallite versus the excitation intensity. The fluorescence count rate of all the observed nanoparticles proves to be proportional to the square of the applied laser power, confirming the presence of the non-linear two-photon process. From Eq. (1), taking  $A_{\text{tot}}$  equal to 0.5%, a value of the two-photon absorption cross section  $\sigma^{(2)}$  of  $(1.1 \pm 0.5) \times 10^{-47} \text{ cm}^4 \text{ s}$  is obtained. Unfortunately, theoretical values for  $\sigma^{(2)}$  for CdS are not known. However for the related semiconductor CdSe a value<sup>24</sup> of  $5 \times 10^{-46} \text{ cm}^4 \text{ s}$  is calculated for nanocrystallites with a similar diameter. The presence of dark periods in the emission on short time scales [as is visible in Fig. 2(c)] will decrease the detected emission rate compared to the ideal two-level representation, thereby possibly explaining the discrepancy between the calculated and experimentally obtained values of  $\sigma^{(2)}$ .

When applying two-photon excitation one should take into account that the selection rules for one-photon and two-photon transitions are essentially different. Two-photon transitions are only allowed between states of equal parity whereas absorption of only one photon gives rise to a change of parity. Moreover, two-photon transitions connect states that differ by two or zero units of  $\hbar$  in their angular momentum whereas for one-photon transitions this difference is one or zero units of  $\hbar$ . Nevertheless, due to the inherent unfeasibility of one-photon fluorescence-excitation spectroscopy of single semiconductor nanocrystallites, two-photon techniques must be considered as a valuable alternative to probe exciton properties that cannot be examined otherwise.

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